Beyond the Chemical Shift

Vibrational Fine Structure in XPS of CO Adsorbed on Ni

The emission of an inner-shell photoelectron leaves a molecule in different vibrational states, thereby causing the peaks of the photoelectron spectrum to divide up into several narrowly spaced peaks (fine structure). It had been assumed that vibrational fine structure for molecules adsorbed on metal surfaces would be broadened by interactions between the molecule and the surface and hence would not be resolvable. High-resolution measurements by a Swedish group at the Advanced Light Source (ALS) have shown that this is not the case. The researchers also observed a detailed dependence of the fine structure on the local geometry of the adsorbed molecule. These results provide a new tool for interpreting x-ray photoelectron spectra of adsorbed molecules.

Core-level (inner-shell) photoelectron spectroscopy (XPS) has been a workhorse of modern surface science. The binding energies of atomic core levels are sensitive to the local chemical environments of the atoms. Utilization of these chemical shifts allows researchers to identify and characterize atoms and molecules adsorbed on surfaces. For example, distinct chemical shifts are found for different substrates and for different adsorption sites. Because core-level ionization in molecules gives rise to an electronic redistribution that modifies the molecular potentials, vibrational excitation can also occur in the core-ionized final state, potentially providing a means to obtain additional information.

In gas-phase measurements, many properties of molecules can be routinely assigned by using the characteristic vibrational fine structure of XPS main lines. But for molecules adsorbed on a metal surfaces, the general assumption has been that the XPS main lines of the adsorbates are broadened by the coupling to the metal. For this reason, no detailed separation of the electronic and vibrational contributions was thought to be possible. The Swedish group's work with CO adsorbed on the nickel (100) surface, however, shows that very small core-level vibrational splittings in adsorbates can be clearly resolved and that electronic and vibrational contributions can be separated.

The analysis of vibrational fine structure in the XPS main lines of adsorbed molecules leads to a significantly enhanced understanding of core-ionized adsorbates. From their data, which clearly show resolvable fine structure due to the CO symmetric stretch vibration in both carbon and oxygen XPS spectra, the group was able to extract information about the electronic (e.g., potential energy surface of the core-ionized molecule) and geometric structure (e.g., change in bond length on core ionization) that exceed what was previously possible with XPS. In general, they were able to extend the powerful tools of vibrational analysis from gas-phase to adsorbed molecules.

On a fundamental level, the researchers confirmed that dynamic metallic screening is of paramount importance in describing core ionization of adsorbates on metals. The XPS main line was found to represent the fully screened final state. Moreover, they could determine the binding energy of the adiabatic transition experimentally, which makes a direct comparison to calculated binding energies easier. In addition, they investigated how the vibrational fine structure of adsorbed CO depends on the substrate and on the adsorption site. From measurements for three different adsorption sites, they could extract the geometric changes upon core ionization of the CO molecule in the different sites.

In sum, these findings provide a line-shape parameterization based on a few physically relevant parameters. In particular, this parameterization relates the XPS line profile to ground-state properties like bond lengths and force constants. The researchers anticipate that this relationship will be useful for researchers trying to interpret core-level photoelectron spectra of adsorbed molecules. However, in order to perform these types of experiments, the high photon flux and high energy resolution of a third-generation synchrotron source are crucial.

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A. Föhlisch, N. Wassdahl, J. Hasselström, O. Karis, D. Menzel, N. Mårtensson, and A. Nilsson, "Beyond the Chemical Shift: Vibrationally Resolved Core-Level Spectra of Adsorbed CO," *Phys. Rev. Lett.* **81** (1998) 1730; A. Föhlisch, J. Hasselström, O. Karis, D. Menzel, N. Mårtensson, and A. Nilsson, "Vibrational Fine Structure in Core Level Photoelectron Lines of Adsorbed Molecules: System Dependent Effects," *J. Electron Spectros. Relat. Phenom.* **101-103** (1999) 303.

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- **Gas-phase core-level photoelectron spectroscopy**
  - *Vibrational fine structure frequently observed and analyzed*
  - *Supplements information available from chemical shift*
- **Molecules adsorbed on metal surfaces**
  - *Vibrational fine structure not expected to be observable*
  - *Interactions with substrate assumed to wash out fine structure*
- **Observation of fine structure for CO/Ni(100)**
  - *Symmetric stretch vibration in both carbon 1s and oxygen 1s spectra*
  - *Confirm that final state is fully screened*
  - *Structure depends on geometry of adsorption site*
- **New tool for interpreting XPS of adsorbed molecules**
  - *Separate and quantify contributions to the line shape*
  - *Line-shape profile related to bond lengths and force constants*
  - *Determine binding energy of adiabatic transition experimentally*

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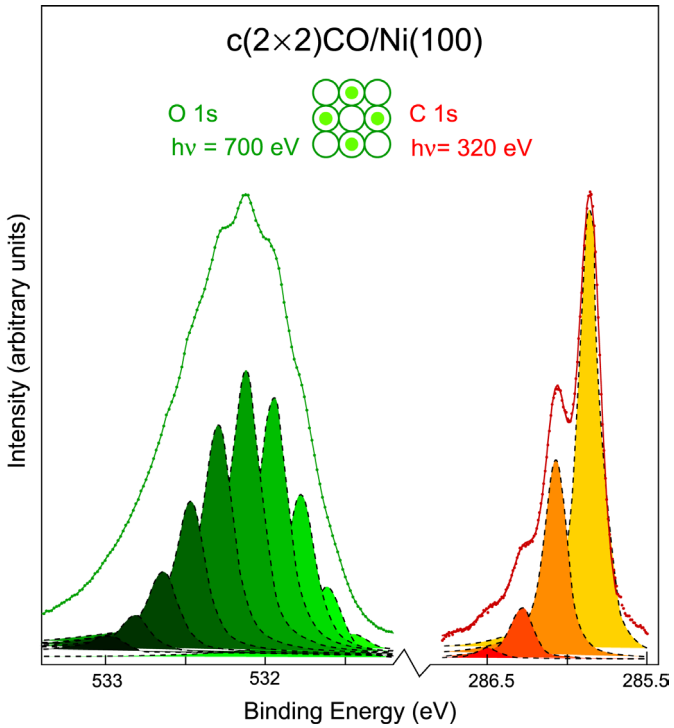

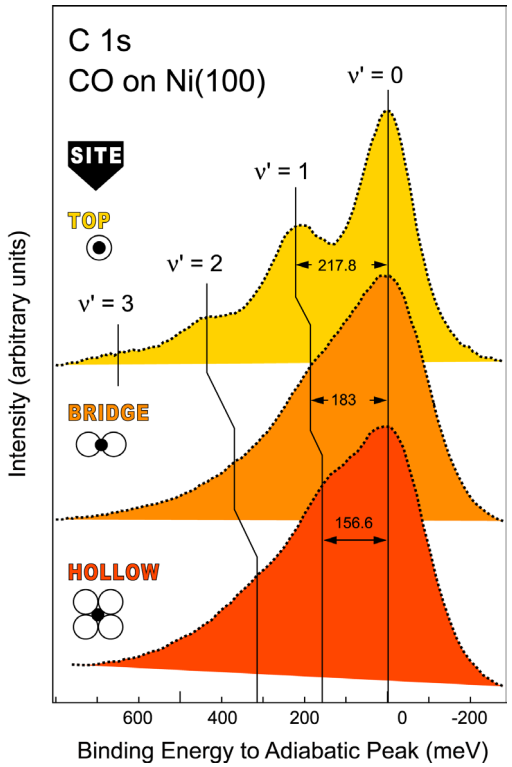

The vibrational fine structure for CO adsorbed on Ni(100) is 217.8 ±2.2 meV for carbon 1s and 173 ±8 meV for oxygen 1s lines.

Carbon-1s vibrational fine structure for CO molecules in top, bridge, and hollow adsorption sites.

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